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Mechanical properties of 2.45 GHz microwave sintered Si_3N_4–Y_2O_3–MgO–ZrO_2 system

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Abstract

Mechanical properties of 2.45 GHz microwave sintered Si_3N_4–Y_2O_3–MgO–ZrO_2 system have been investigated. Microwave sintered samples exhibited higher hardness compared to conventionally sintered samples. SEM microstructures of microwave sintered samples revealed lower average grain length and width than those of the conventionally sintered samples. Fracture toughness increased with increasing sintering temperature in the case of conventionally sintered samples whereas microwave sintered samples exhibited no variation despite differences in microstructure. The results of present study demonstrated that microwave sintering could influence the microstructure and thereby improve the mechanical properties.

Keywords: Silicon nitride; 2.45 GHz microwave sintering; Microstructure; Vickers hardness

1. Introduction

Silicon nitride is one of the most promising high-temperature structural material due to its high-temperature thermal and mechanical properties.[1] Mechanical properties such as strength, hardness and fracture toughness control of Si_3N_4 has been difficult due to the relatively complex microstructure developed during densification by liquid-phase sintering and the complicated interrelationships between the size and shape of the silicon nitride grains, distribution of the grain boundary phase, and the mechanical properties.[2,3] The multi-phase microstructure of elongated β-Si_3N_4 crystals embedded in an amorphous or partially crystalline grain boundary provides a great opportunity to optimize material properties for specific applications. Therefore, tailoring of microstructure is required to improve mechanical and thermal properties.[4]

Large elongated grains are necessary but not sufficient by themselves for high toughness.[5] Interfacial bonding force between grains and glass phase is another key factor, and thus the chemistry of grain boundary phase is also important.[6] Appropriate starting powders, compositions and sintering methods are required to optimize the microstructure and properties.[7] For instance, grain growth is promoted by high-temperature sintering (gas pressure sintering) and selecting suitable sintering additives which promote grain growth.[8] On the other hand, low-temperature sintering and a grain growth inhibitor is necessary to obtain high-strength materials. Recently microwave sintering attracted much attention of many researches due to its capability of volumetric heating, high heating rate, and producing unique microstructures.[9–11]

There have been several studies dealing with the sintering of silicon nitride using microwave energy.[12–16] Plucknett and Wilkinson[12] microwave sintered silicon nitride in air with a typical sintering time of 90 min, although longer cycle times were used for larger batches (1 kg). Y_2O_3 and Al_2O_3 were used as sintering additives, and a density of 3.10 (94% of theoretical density) was achieved. Patterson et al.[13] microwave sintered 1 kg of silicon nitride with 5 wt% each of Y_2O_3 and Al_2O_3; full density was achieved by hipping at 1800 °C for 60 min. They reported energy savings up to 78% with microwave sintering. Tiegs et al.[14] successfully conducted microwave sintering of silicon nitride with 12 wt% Y_2O_3 and 4 wt% Al_2O_3; after sintering at 1750 °C for 1 h, a density of 96% was obtained. They also observed that incorporation of secondary additives that couple well with microwaves such as SiC and TiN to silicon nitride enhanced the densification processes.[15] Hirota et al.[16] sintered silicon nitride using 28 GHz frequency and reported 97% theoretical density and fracture toughness of 9 MPa $m^{1/2}$.

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Recently Jones et al.[17] sintered Si_3N_4 using 28 GHz microwave using MgO, Y_2O_3 and Al_2O_3 as sintering additives and achieved indentation fracture toughness 6 MPa $m^{1/2}$ and hardness of 14 GPa. Getman et al.[18] sintered silicon nitride using 30 GHz microwave frequency with 3 wt% Al_2O_3, 5 wt% Yb_2O_3 at 1750 °C and reported fracture toughness of 9.5 MPa $m^{1/2}$ and hardness of 15.4 GPa. However, microwave systems operating at 30 GHz are not cost effective for industrial heating applications. Therefore, the objective of this research was using 2.45 GHz microwave furnace to sinter Si_3N_4 by carefully selecting microwave absorbing sintering additives based on temperature dependent dielectric properties. The sintering additives selected for the present study were MgO, Y_2O_3, and ZrO_2. The results of grain size analysis, indentation fracture toughness and Vickers hardness were compared to those with conventionally sintered samples with identical sintering temperature but different dwell time and heating rates.

1.1. Experimental procedure

The silicon nitride samples were prepared with α-Si_3N_4 powder (E10 grade, UBE Industries Ltd., Yamaguchi, Japan) with 6 wt% Y_2O_3 (Aldrich Chemical Company Inc., Milwaukee, WI, 99.99%), 4 wt% MgO (Aldrich Chemical Company Inc., Milwaukee, WI, 99.99%), and 2.5 wt% of TZ3Y(3 mole% Y_2O_3 stabilized ZrO_2, Tosoh Corporation, Tokyo, Japan, 99.99%). The powders were ball milled in de-ionized water for 12 h using high wear resistant ZrO_2 milling media (YTZ Grinding Media, Tosoh Corporation, Tokyo, Japan). The dried powders were ground and sieved through a 38 μm mesh. Five grams of the mixed powder were die-pressed at 30 MPa and cold isostatically pressed at 200 MPa into cylindrical green pellets of diameter 23 mm and thickness of 5 mm. Microwave sintering was carried out in a 2.45 GHz, industrial microwave furnace with variable output power of maximum 3 kW. Sintering trials were performed at three different temperatures at 1650 °C, 1700 °C and 1750 °C respectively with a dwell time of 15 min. On the other hand, conventional sintering trials were performed at similar temperatures with a dwell time of 60 min. A detailed description of microwave sintering setup details have already been described elsewhere.[19] Phase analysis was carried by XRD (Philips, XRG 3100 X-ray generator, Almelo, The Netherlands). The generator was set to 40 kV and 20 mA utilizing CuKα radiation. XRD patterns were analyzed using a software package JADE 7 (Materials Data, Livermore, CA). XRD peak height of [2 1 0] of β-Si_3N_4 was compared with [2 1 0] of α-Si_3N_4 to determine the relative amounts of α and β phases present in the silicon nitride samples as described by Gazzara and Messier.[20] The method reduces the effects of preferred orientation and the influence of particle size thereby eliminating the errors associated with common measurements. The microstructures were evaluated from diamond polished and CF_4 plasma etched samples using FEG 200 (FEI Company, Hillsboro, OR) environmental SEM (ESEM) with a field emission gun (FEG) operating at 10 kV. The same specimens were used to measure Vickers indentation fracture toughness, under a load of 98 N, using the equation.

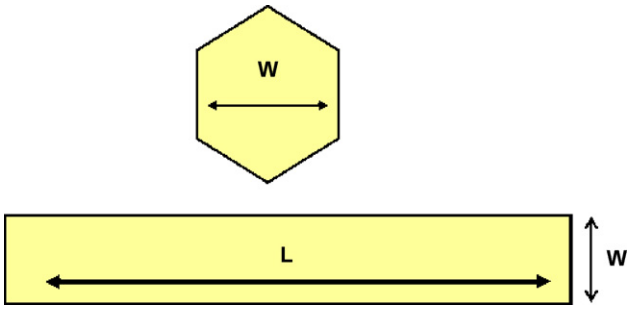

Fig. 1. Grain size parameters as determined from specific grain sections.[21] "*L*" represents length of grain and "*w*" represents width or diameter of the grain.

$$K_c = 0.016\left(\frac{E}{H}\right)\left(\frac{P}{c^{3/2}}\right) \quad (1)$$

where E is the Young's modulus, H is the hardness, P is the peak load and c is the crack length. The crack lengths were measured using optical microscope after making indents on the samples.

Grain size analysis was performed based on the method described by Kramer et al.[21] Enlarged SEM micrographs were used to measure the length and width of individual grains with the help of image analysis by marking grain boundaries prior to measurement. These measurements were used for the determination of dimensional parameters which describe the individual β-Si_3N_4 grain morphology, such as length, width and aspect ratio. At least 1000 grains were measured for each sample to obtain reliable results. Since β-Si_3N_4 grains grow without impingement, they form ideal hexagonal prisms which can be characterized by length (L) and width (W). The width is defined as the distance between opposite but parallel planes and can be determined accurately from arbitrary sectioned prisms, as shown in Fig. 1. When the section is not parallel to the c-axis of the prism, the measured length is somewhat larger than the true length. Nevertheless, the error is small for aspect ratios larger than 1.5. In the present study, aspect ratio values more than 1.5 were used for plotting aspect ratios versus frequency of silicon nitride samples.

2. Results and discussion

Silicon nitride samples with composition of 87.5 wt% Si_3N_4, 6 wt% Y_2O_3, 4 wt% MgO and 2.5 wt% ZrO_2 were sintered at different temperatures in the range of 1650 °C up to 1750 °C in a flowing nitrogen atmosphere. A theoretical density of 95% was achieved within 75 min of microwave sintering with a hold time of 15 min at the sintering temperature of 1750 °C. Comparable density was achieved only after 60 min of hold time at 1750 °C with a heating rate of 10 °C/min in the case of conventional sintering. Table 1 shows the XRD intensity ratios of α- and β-Si_3N_4 samples sintered using both microwave and conventional techniques. The X-ray results show that α → β phase transformation completed at a lower sintering temperature of 1650 °C for 15 min in the case of microwave sintered samples.

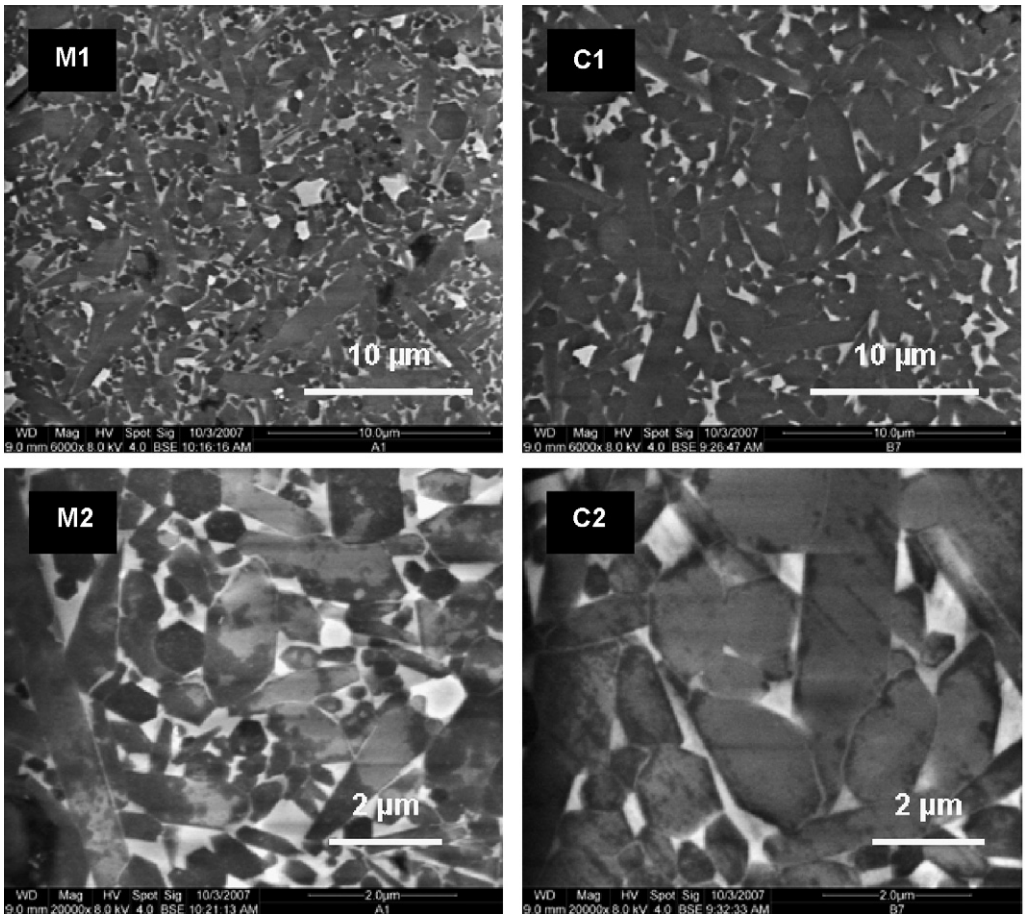

Fig. 2. SEM micrograph, M1 represents the microwave sintered sample at 1750 °C for 15 min and M2 is the magnified image of M1. The micrograph, C1 represents conventionally sintered sample at 1750 °C for 60 min and C2 is the magnified image of C1.

On the other hand, phase transformation is not completed even at 1750 °C for 60 min in the case of conventionally sintered sample. The complete phase transformation observed in microwave sintered samples is attributed to the localized heating within the grain boundary phase which in turn increased the rate of dissolution of α-Si_3N_4 phase and re-precipitated as β-Si_3N_4 crystals.[22] An alternative possible explanation for the phase transformation at lower temperature in the case of microwave sintered samples may be due to error introduced in the temperature measurement using optical radiation pyrometer, where the temperature is monitored at the surface of the samples while the temperature at center of the sample is much higher due to reverse thermal gradients usually observed in microwave heating.[23]

Fig. 2 shows a comparison of the microstructures of microwave and conventionally sintered samples at 1750 °C. A typical bimodal grain size distribution is evident in the micrographs. All the samples revealed grain morphology of either hexagonal or rectangular shapes and no rounded shaped alpha silicon nitride was found, confirming that α → β phase transformation of silicon nitride was completed. Results of distributions of grain length, width and aspect ratio of a specimen sintered at 1750 °C are shown in Fig. 3. One can clearly see that the grain sizes of conventionally sintered samples are larger than microwave sintered sample. The mean grain length is 1.7 μm and width is 0.69 μm for microwave sintered samples at 1750 °C for 15 min and 3.1 μm and 0.73 μm for conventionally sintered samples at 1750 °C for 60 min. Aspect ratios of conventionally sintered samples exhibited 3 peaks at 2 μm, 3 μm and 4 μm respectively indicating bimodal grain size distributions. On the other hand, microwave sintered sample revealed one prominent peak at 3 μm with small number of elongated β-Si_3N_4 grains. The difference in microstructure of conventional and microwave sintered samples can be explained on the basis of Kingery's[24] three-stage model for liquid-phase sintering. The initial stage of particle rearrangement is caused by the initial formation of liquid. It may be possible that the selective localized microwave heating decreases the viscosity of grain boundary glassy phase and enhances the rearrangement of particles under the action of surface tension. The second stage is solution–precipitation process in which material is dissolved away from particle contact

Table 1
XRD intensity ratios of microwave and conventional sintered β-Si_3N_4 as a function of sintering temperature (T, °C).

T (°C)	$\beta_{(210)}/(\beta_{(210)}+\alpha_{(210)})$	
	Microwave	Conventional
1650	1	0.73
1700	1	0.75
1750	1	0.81

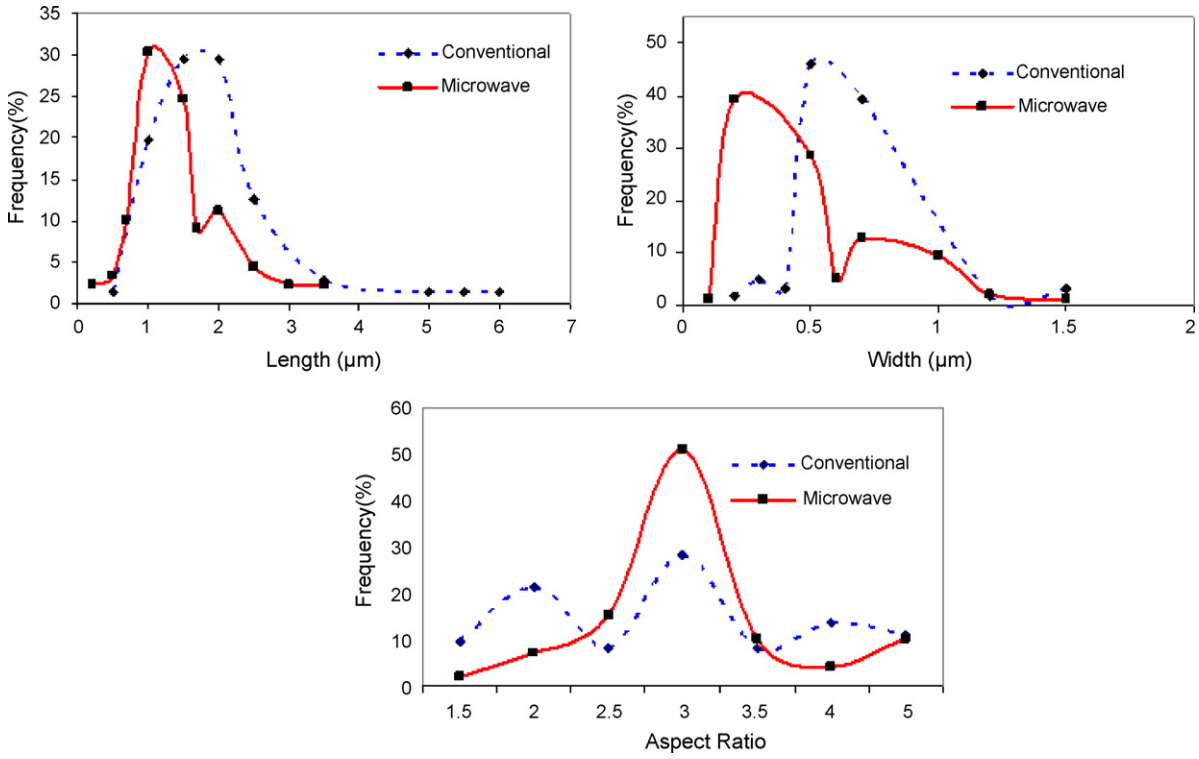

Fig. 3. Measured grain lengths, widths and aspect ratios of microwave and conventionally sintered samples at 1750 °C in flowing N_2 atmosphere.

points, causing their centers to approach each other. Microstructural coarsening by ostwald ripening dominates during the final stage of sintering. Broad distribution of length and width indicates that the grain growth mechanism reconciles with the diffusion controlled ostwald ripening results from dissolution of the smaller grains and precipitation of the larger grains.[25] The microstructural analysis shows that third stage of liquid-phase sintering, ostwald ripening is influenced by microwave sintering. It seems to be the longer holding time of 60 min in the case of conventionally sintered samples at the sintering temperature was responsible for the larger grain size compared to microwave sintered fine grained microstructure due to shorter holding period of 15 min. Another plausible explanation is that the complete phase transformation occurred at a lower temperature of 1650 °C prevented further grain growth since the phase transformation and grain growth occur simultaneously at initial stages of densification.

Similar observations were previously reported by many researchers.[12,26,27] These researchers used Y_2O_3 and Al_2O_3 as sintering additives and correlated the fine grain microstructure to volumetric heating of microwaves. In contrast, there were also reports of enhanced grain growth in microwave sintered silicon nitride. Tiegs et al.[15] observed elongated β-Si_3N_4 when they used Y_2O_3 and Al_2O_3 sintering additives along with SiC or TiN as secondary additives. On the other hand, Hirota et al.[16] used rare earth sesquioxide sintering additives and observed similar trends. Based on the collective results, it is becoming clear that the microwave effect is not likely the only factor influencing the enhanced β-Si_3N_4 grain growth, but also the choice of densification additives as observed by Becher et al.[28] in their recent study of the effect of rare earth sintering additives on the microstructure evolution of conventionally sintered silicon nitride.

The Vickers indentation hardness of microwave and conventionally sintered samples as a function of sintering temperature is shown in Fig. 4. The measured hardness values of microwave sintered samples increased with increasing sintering temperature while conventional sintered samples showed a decreasing tendency at 1750 °C. Although there was a slight decrease of hardness with temperature in the case of conventional sintered samples, this is negligible in comparison with microwave sintered samples. It is a well known fact in a ceramic material that hardness decreases with porosity.[29] Therefore, in our present study the observed increase in hardness with increasing sintering temperature in the case of microwave sintered samples is correlated with decrease in porosity as revealed by the density data presented in Fig. 5. One can clearly see that density of microwave sintered sample increased with increasing tem-

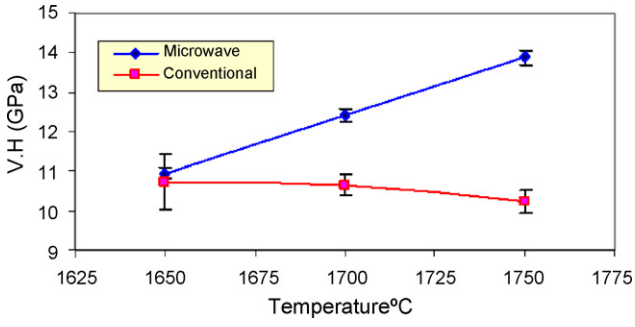

Fig. 4. Measured Vickers Hardness of microwave and conventional sintered samples as a function of sintering temperature.

Table 2
Comparison of mechanical properties of microwave sintered silicon nitride.

Frequency (GHz)	Sintering temperature (°C)	Sintering additives	Vickers hardness (GPa)	Fracture toughness (MPa $m^{1/2}$)	Authors
28.0	1450–1850	Y_2O_3, Al_2O_3, MgO	14	6	Jones et al.[17]
30.0	1780	Al_2O_3, Yb_2O_3	15.4	9.5	Getman et al.[18]
2.45	1700–1800	Al_2O_3, Y_2O_3	17.1	5.5	Plucknett and Wilkinson[30]

perature while the conventional sintered samples showed no significant variation. The most striking feature of the mechanical properties of microwave sintered specimens were the higher hardness value compared to conventional sintered sample with identical density. The hardness value of microwave sintered samples (~14 GPa) was significantly greater than the conventionally sintered sample (~10 GPa). These differences could be due to different microstructure as evident by the grain size analysis. Microwave sintered samples exhibited fine grain structure compared to conventionally sintered samples. Similar observation has previously been reported by many researchers.[17,18,30] The mechanical properties and sintering conditions were illustrated in Table 2. Jones et al.[17] sintered Si_3N_4 using 28 GHz microwave and achieved indentation fracture toughness 6 MPa $m^{1/2}$ and hardness of 14 GPa. Getman et al.[18] sintered silicon nitride using 30 GHz microwave frequency and reported fracture toughness of 9.5 MPa $m^{1/2}$ and hardness of 15.4 GPa. Plucknett and Wilkinson[30] reported hardness value of 17 GPa for the silicon nitride sintered using 2.45 GHz microwave energy followed by HIPing at a temperature of 1800 °C with a pressure of 200 MPa for 1 h and claimed that fine grain microstructure with an average grain diameter of 200 nm was responsible for the higher hardness value. Hirano et al[31] argued that the decrease in hardness of Si_3N_4/SiC was due to the increase in Si_3N_4 grain size. Coe et al.[32] found an inverse relationship between hardness and grain size in the case of hot pressed Si_3N_4. Xu et al.[33] sintered nano-sized Si_3N_4 using spark plasma sintering (SPS) at 1600 °C for 5 min at a heating rate of 300 °C/min and obtained elevated hardness and the authors correlated the high hardness value with fine grain structure (70 nm).

The results of indentation fracture toughness measurements are presented in Fig. 6. There was a slight increase in toughness with temperature in the case of conventional sintered samples due to large grain size of β-Si_3N_4 compared to microwave sintered samples. However no significant variation was observed in the microwave sintered samples despite differences in microstructures. It is also interesting to note that the samples with only 89% density have comparable toughness to 95% dense samples. One can explain the above observed result based on the limitation of Vickers Indentation Fracture Toughness test (VIF Test) recently reviewed by George Quinn and Richard Bradt.[34] The authors clearly pointed out that VIF does not provide any meaningful information about the crack arrest situation because of the complex nature of the interacting stress field. The extensive crack pattern beneath the surface, where indentation begins is not represented in the formula used in our calculation of fracture toughness leads to unreliable results. Internationally accepted standardized fracture toughness tests, for ceramics such as chevron-notched beam (CNB) test or single-edge-pre-cracked beam (SEPB) tests needs to be performed on the samples to get accurate results.[34] Fig. 7. shows the indentation crack profiles of microwave sintered Si_3N_4 at 1750 °C. The inset clearly shows transgranular and intergranular crack profiles. The conventional sintered samples also exhibited similar crack growth behavior as indicated in Fig. 8. There is a wide body of knowledge on the effect of grain boundary phase on the crack propagation mode.[6,35] Kleebe et al[6] reported that secondary-phase chemistry plays a dominant in controlling the interfacial debonding which in turn determine whether the crack advance in transgranular or intergranular mode.[6] Very recently, Kruzic et al.[35] reported that RE elements with large ionic radius (e.g., La) results weaker grain boundary adhesion leading to intergranular fracture and RE elements with small ionic radius (e.g., Lu) results stronger grain boundary adhesion leading to transgranular fracture. Tanaka et al.[36] studied the effect of grain boundary phase on toughness and crack propagation. They reported a fracture toughness of 3 MPa $m^{1/2}$ for their fully dense material without additional sintering aids. The addition of 20 vol% silicon nitride whiskers raised the fracture

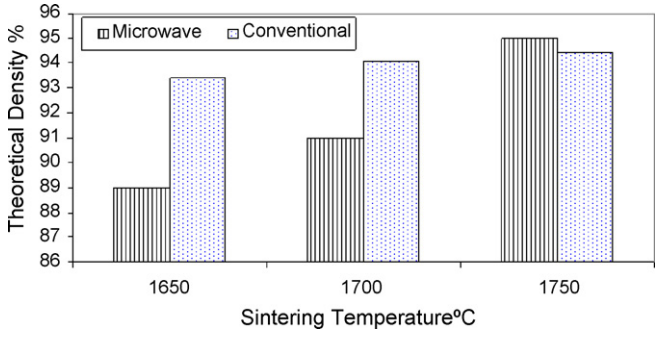

Fig. 5. Density of microwave and conventional sintered samples as a function of sintering temperature.

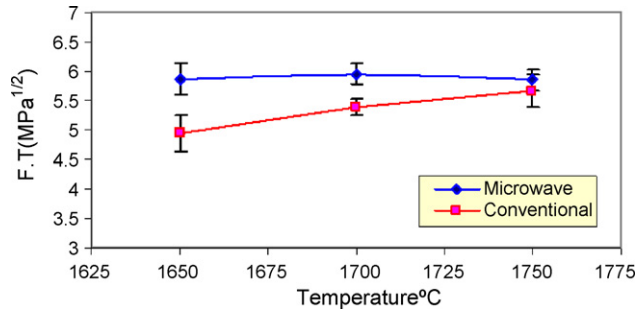

Fig. 6. Measured indentation fracture toughness of microwave and conventional sintered samples as a function of sintering temperature.

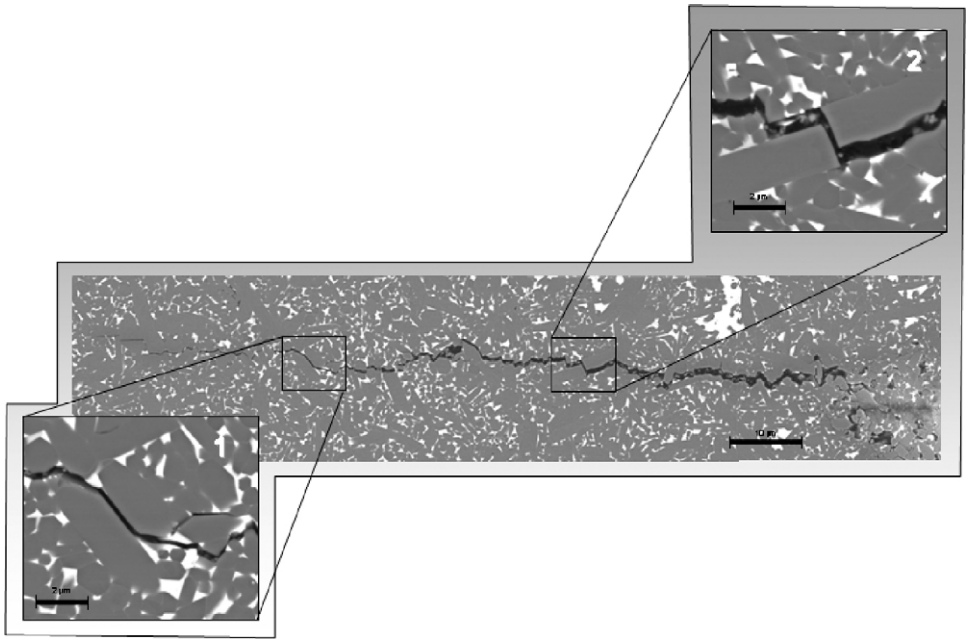

Fig. 7. Crack paths of microwave sintered Si_3N_4 at 1750 °C in flowing N_2 atmosphere. Inset-1 shows intergranular crack propagation and inset-2 shows transgranular crack propagation.

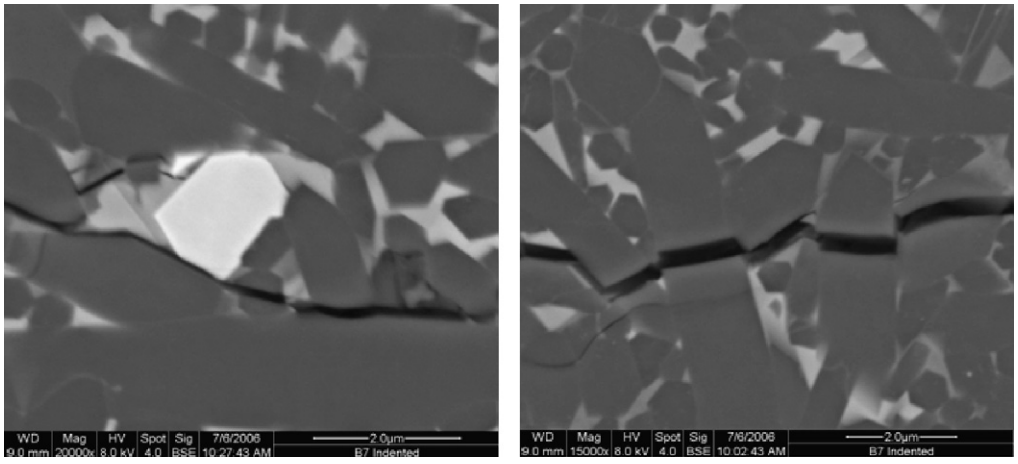

Fig. 8. Crack paths of conventional sintered Si_3N_4 at 1750 °C in flowing N_2 atmosphere.

toughness only slightly, up to 3.5 MPa $m^{1/2}$. They also observed nearly transgranular fracture, with little sign of crack bridging, deflection, or pullout by the whiskers.[37] Thus, their study shows that, the whiskers did not contribute much to the fracture toughness. Kleebe et al.[6] further clarified that, secondary-phase chemistry is the dominant parameter which governs the toughening mechanism of liquid-phase-sintered silicon nitride materials and microstructural parameters such as grain diameter or apparent aspect ratio are considered to be of secondary importance. Peterson and Tien[38] investigated the effect of grain boundary thermal expansion coefficient on the fracture toughness in silicon nitride and concluded that at low temperature the effect of sintering aid chemistry on grain morphology was negligible. Based on the above arguments, one can relate the existence of both transgranular and intergranular mode of crack propagation in the present study may be related to the non-uniform distribution of sintering additives at grain boundaries with in the sample.

3. Conclusions

The indentation fracture toughness of microwave sintered silicon nitride samples was not significantly different from conventionally sintered samples despite differences in microstructures. Microwave and conventional sintered samples exhibited both transgranular and intergranular crack profiles. Microwave sintering favored fine grained β-Si_3N_4 compared to conventional sintering with identical sintering temperatures but different heating rate and dwell times. The enhanced Vickers hardness observed in the case of microwave sintered samples is

most likely due to the fine grain microstructure developed by the rapid heating rate of 50 °C/min versus 10 °C/min in the case of conventional sintering.

Acknowledgments

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